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## Validity of rigid band approximation of PbTe thermoelectric materials

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The tuning of carrier concentration through chemical doping is very important for the optimization of thermoelectric materials. Traditionally, a rigid band model is used to understand and guide doping in such semiconductors, but it is not clear whether such an approximation is valid. This letter focuses on the changes in the electronic density of states (DOS) near the valence band maximum for different *p*-type dopants (Na, K, Tl, or vacancy on Pb site) maintaining the high symmetry of the NaCl structure. Na- and K-doped, and vacancy-introduced PbTe show a clear rigid-band like change in DOS unlike that concluded from supercell based calculations. © 2013 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License. [<http://dx.doi.org/10.1063/1.4809545>]

Thermoelectrics, which can generate power through the direct conversion of heat energy into electrical energy, are an attractive strategy of saving electricity from waste-heat recovery toward a solution to the global energy demands. To attain high energy conversion efficiency, thermoelectric materials should have a large dimensionless figure of merit,  $zT$ , defined as  $zT = S^2 \sigma T / \kappa$ , where  $S$ ,  $\sigma$ ,  $\kappa$ , and  $T$  are the Seebeck coefficient, electrical conductivity, thermal conductivity, and temperature, respectively.<sup>1,2</sup> For the practical application of thermoelectric materials,  $zT$  is desired to be above at least unity. To obtain a high  $zT$ ,  $S$  and  $\sigma$  should be optimized as large as possible while  $\kappa$  should be minimized. There are two primary strategies to enhance  $zT$ . One is optimizing the electronic portion,  $S^2 \sigma$ , which is mainly governed by the local electronic structure near the Fermi level.<sup>3</sup> The other attempt is lowering  $\kappa$  by introducing phonon scattering such as mass contrast<sup>4</sup> and nanostructure<sup>5</sup> in bulk materials.

Lead telluride (PbTe) with rocksalt (NaCl) type crystal structure is a well-known semiconductor material used for thermoelectric power generation, and recently the reasons for its high  $zT$  are studied experimentally.<sup>6–23</sup> The high  $zT$  can be understood by the effects of resonant states near the band edge,<sup>6,9,15,16</sup> the complex band structure and band engineering,<sup>10–14,17–19</sup> the introduction of nanostructures,<sup>5,20–23</sup> or a combination thereof.

From the theoretical point of view, the electronic and peculiar phonon structure of PbTe has been studied extensively.<sup>24–26</sup> In particular, the valence band of PbTe is known to have a complex structure<sup>27–29</sup> that is often interpreted as consisting of two valence bands or a complex Fermi surface. Regardless of the exact band structure, it is generally assumed that the electronic band structure is relatively rigid, unless impurity states are involved. In other words, the electronic structure of doped PbTe can be effectively approximated as that of pure PbTe, provided an appropriate Fermi level is used. Such a rigid band approximation is usually a valuable approach for understanding doped semiconductors, and any significant deviation from this approximation would profoundly affect the transport properties, and therefore requires a careful reevaluation.

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Ahmad *et al.* have reported the effects of hole- and electron-doping with various kinds of dopants on the electronic structure for PbTe using a supercell method based on *ab initio* calculation.<sup>30</sup> They find that the transport properties can be significantly affected beyond that predicted by a simple rigid band approximation because the electronic density of states (DOS) in the conduction and valence bands is perturbed by dopants or defects.<sup>30,31</sup> On the other hand, Singh *et al.* have shown that rigid band approximation can reproduce the experimental thermoelectric properties,<sup>28,32</sup> considering that the bands are known to be complex and non-parabolic.<sup>11,28,30–32</sup> However, one complication is that a supercell model<sup>28–34</sup> reduces the crystal symmetry, while no loss of symmetry is normally observed in experimental X-ray or electron diffraction experiments. While real systems neither maintain perfect symmetry nor transform into perfect supercells, it is important to understand the effect of symmetry on the band structure.

To investigate the doping effects on the band structure without reducing crystal symmetry, we performed calculations using the Korringa-Kohn-Rostoker Green function formalism under the coherent potential approximation (KKR-CPA) developed by Akai *et al.*<sup>35–37</sup> The KKR-CPA calculation is a powerful method to calculate the band structure for disordered materials without requiring a supercell, that is, neither the symmetry nor the size of the unit-cell has to be changed. The KKR-CPA method has been successfully applied to explain experimental data in PbTe doped with both resonant and non-resonant impurities.<sup>9,15,38,39</sup>

To test the validity of the rigid band approximation for Na- and K-doped PbTe, which has been used to explain the experimental data successfully, we calculated various amounts of doping with Na and K on Pb site, that is, up to 10% although the experimental upper limit would be less than  $\sim 2\%$ .<sup>8,11,18</sup> Furthermore, we compared with Tl-doping, which is reported to form resonant impurity states<sup>6,9,15</sup> in the vicinity of the valence band maximum and to exhibit superconducting properties.<sup>40,41</sup> Also, we reexamined the effects of vacancy on Pb site.<sup>30</sup> Comparing these impurities will allow a test of the validity of the rigid band approximation for *p*-type doped PbTe thermoelectric material using a calculation method without changing the symmetry of the crystal structure. In most calculations, a constant room-temperature lattice constant of 6.462 Å (12.22 bohrs)<sup>42</sup> is used to examine the doping effects only. The change in lattice parameter is known to alter the band structure, particularly the bandgap. In all calculations, the von Barth-Hedin formula<sup>43</sup> for the exchange energy was used. The effect of spin-orbit interactions (SOI) is not included in the method used here as described in Ref. 39. While SOI has a significant influence in PbTe on the absolute energy calculated, as discussed in detail in Ref. 44, the purpose here is to analyze only relative differences due to doping.

Figure 1 shows the calculated DOS for  $\text{Na}_x\text{Pb}_{1-x}\text{Te}$ ,  $\text{K}_x\text{Pb}_{1-x}\text{Te}$ ,  $\text{Pb}_{1-x}\square_x\text{Te}$ , and  $\text{Tl}_x\text{Pb}_{1-x}\text{Te}$  with  $x = 0$  and 0.025, where  $\square$  is a vacancy on the Pb Site. The overall shape of the DOS for pure PbTe ( $x = 0$ ) is consistent with the previous KKR-CPA results.<sup>9,15,38</sup> The shape of both the valence and conduction bands is not changed significantly via doping with Na, K, nor by introducing vacancies on Pb site, but the bandgap slightly increases. In all cases, the Fermi level drops into the valence band in accordance with the expected chemical effect of one hole introduced by each substitutional monovalent Na, K, Tl, or two holes for each Pb vacancy,<sup>30</sup> which has also been observed experimentally by low temperature Hall coefficient measurements.<sup>4,10,14,45,46</sup>

In contrast to Na, K, and  $\square$  substituting Pb, Tl doping forms additional states near the valence band maximum, described as resonant impurity states. The importance of SOI and complicated effect of Tl are discussed in detail.<sup>9,15,28,30,44</sup> Here, we confirmed that strong effects of Tl are also observed in KKR-CPA calculations.<sup>9,15</sup> The resonant impurity states can be attributed to Tl *s*-states, because the DOS modification occurs at the energy of Tl 6*s* states (shown in Fig. 1) and the magnitude increases with increasing Tl concentration, as shown in Fig. 2. The resonant impurity states may contribute to the large  $zT$  up to 1.5 at 773 K in *p*-type Tl-doped PbTe.<sup>6,9</sup> The different effects of Tl and Na on the transport properties including DOS mass and mobility are discussed in Refs. 11 and 19.

The difference among the resonant dopant Tl and the strikingly similar behavior of Na, K, and vacancy is seen in the analysis of the bandgap (Fig. 3). The addition of Tl reduces the bandgap in a non-linear manner due to the formation of resonant impurity states in the vicinity of the valence band maximum. By Na and K doping or introducing vacancy on Pb site, the bandgap increases

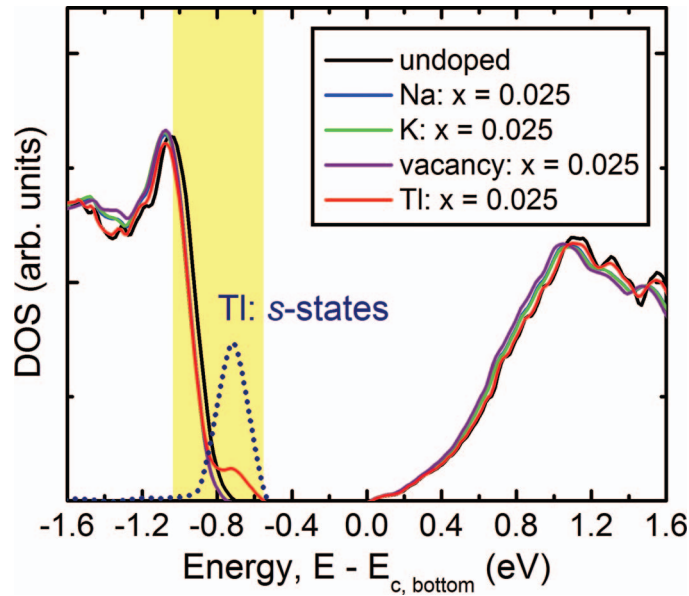


FIG. 1. Electronic density of states (DOS) for Na-doped, K-doped, vacancy-introduced, and Tl-doped PbTe [(Na, K, □, Tl)<sub>x</sub>Pb<sub>1-x</sub>Te ( $x = 0.025$ )]. The dotted line shows the partial DOS of Tl *s*-states. The energy window was set within 0.5 eV from the top of the valence band.

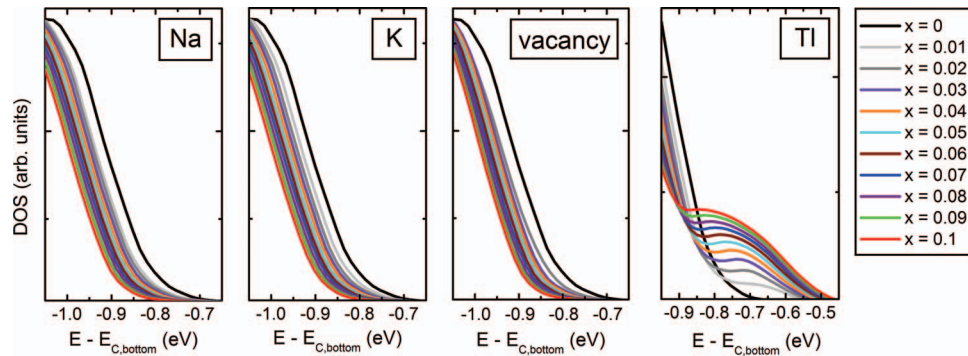


FIG. 2. Electronic density of states (DOS) near the valence band maximum for Na-doped, K-doped, vacancy-introduced, and Tl-doped PbTe [(Na, K, □, Tl)<sub>x</sub>Pb<sub>1-x</sub>Te ( $0 \leq x \leq 0.1$ )].

slightly with increasing doping concentration. We only show the data with  $x$  up to 0.025 for clarity in Fig. 3 because the experimental doping limit exhibiting high  $zT$  would be  $\sim 2\%$  as shown for Na- and K-doped PbTe.<sup>8,11,18</sup> For pure PbTe ( $x = 0$ ), the estimated bandgap of 0.67 eV is larger than that of the experimental measurements ( $\sim 0.2$  eV),<sup>47</sup> but is consistent with the previous KKR-CPA result of 0.68 eV.<sup>38</sup> Although the magnitude of the estimated bandgap is large compared with experiment ( $\sim 0.2$  eV), the trend with changing the doping concentration can be qualitatively compared.

The DOS of Na, K, and vacancy is strikingly similar to pure PbTe, suggesting that the rigid band approximation should be reasonably valid for these dopants if the NaCl-type crystal symmetry is maintained. In Fig. 2, we show the doping concentration dependence of the DOS within 0.4–0.5 eV from valence band maximum for Na<sub>x</sub>Pb<sub>1-x</sub>Te, K<sub>x</sub>Pb<sub>1-x</sub>Te, Pb<sub>1-x</sub>□<sub>x</sub>Te, and Tl<sub>x</sub>Pb<sub>1-x</sub>Te ( $0 \leq x \leq 0.1$ ). The DOS in this energy range should have a critical influence on the transport properties of *p*-type samples. From the KKR-CPA calculations, we can see that Na doping, K doping, or introducing vacancies on the Pb site does not modify the shape of the DOS with  $x$  up to 10%. This clearly suggests that the rigid band approximation should be applicable in these systems. However, the

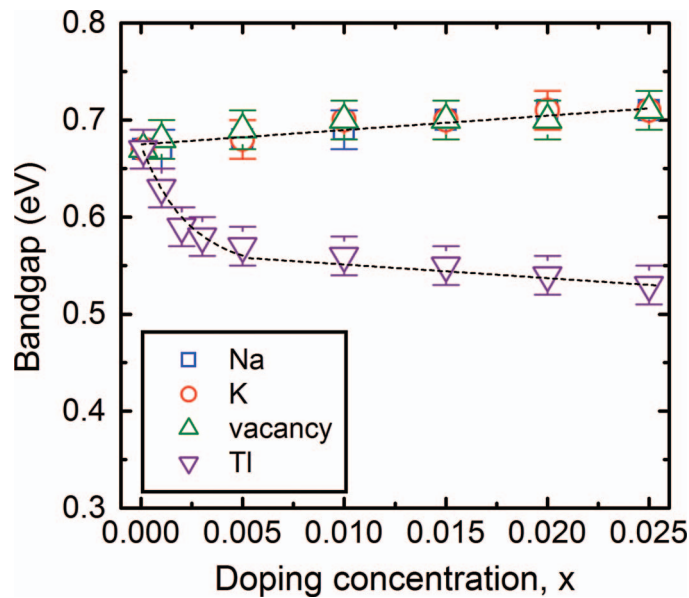


FIG. 3. Bandgap for Na-doped ( $\text{Na}_x\text{Pb}_{1-x}\text{Te}$ ), K-doped ( $\text{K}_x\text{Pb}_{1-x}\text{Te}$ ), vacancy-introduced ( $\text{Pb}_{1-x}\square_x\text{Te}$ ), and Tl-doped PbTe ( $\text{Tl}_x\text{Pb}_{1-x}\text{Te}$ ) ( $0 \leq x \leq 0.025$ ). The dashed lines are drawn to guide the eye.

strongly perturbed DOS from Tl doping in energy range,  $-1.0 \text{ eV} < E - E_{\text{C, bottom}} < -0.5 \text{ eV}$ , is very different from the case of Na, K doping, and introducing vacancy on Pb site. Thus, the simple rigid band approximation is not expected for Tl doping. The effect of the lattice parameter<sup>8</sup> was also investigated, but a small change of 0.1% in lattice parameter in Na or K substitution has an unnoticeable effect on the DOS as shown in Fig. 2.

If the high symmetry of the NaCl structure is broken by doping or alloying, then the band structure changes and leads to significant differences in DOS and bandgap.<sup>30,32,48</sup> Experimentally, the NaCl structure is maintained according to X-ray diffraction in the solid-solution region of these and most other alloys and dopants of IV-VI compounds. At an atomic scale near the dopants, however, the local symmetry will differ from the perfect NaCl, and some effects of scattering and DOS alterations are expected.

In summary, we demonstrated the KKR-CPA calculation to check the validity of the rigid band approximation for randomly disordered Na-, K-, and Tl-doped, or vacancy-introduced PbTe *p*-type thermoelectric material, in terms of doping concentration dependence of the DOS and bandgap. We confirmed that Na doping, K doping, or introducing vacancy on Pb site shows a rigid band like behavior on the DOS, unlike Tl doping which forms clear resonant impurity states in the vicinity of the valence band maximum. Therefore, the KKR-CPA method is believed to be an effective approach to check the accuracy of the rigid band approximation, which is usually applied in PbTe.

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